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FAST MULTIPOLE METHOD IN SIMULATIONS OF AQUEOUS SYSTEMS

by

James N. Glosli
Michael R. Philpott

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IBM Research Division, Almaden Research Center,
650 Harry Road, San Jose, CA 95120-6099

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As an application of fmm we describe it's use with constant temperature molecular dynamics to calculate the dielectric constant of the spce water model in bulk at temperatures 298K and 361K. System sizes of 27, 64, 125 and 216 water molecules were considered. Comparison with the Ewald and reaction field methods was made. At 298K the dielectric constant was calculated to be $\varepsilon=75.5\pm5\%$ and at 361K $\varepsilon=57.3\pm4\%$. Both values compare well with experiment and the reaction field theory simulations.

FAST MULTIPOLE METHOD IN SIMULATIONS OF AQUEOUS SYSTEMS

James N. Glosli and Michael R. Philpott
IBM Research Division, Almaden Research Center
650 Harry Road, San Jose, CA 95120-6099

Abstract

The fast multipole method (fmm) for calculating electric fields developed by Greengard and Rokhlin (J. Comp. Phys. 73, 325(1987)), has been implemented specifically for molecular dynamics simulations of electrochemical problems including boundary conditions associated with metal electrodes. This order N (number of charged particles) algorithm, is known to be computationally much more efficient than direct or Ewald sum methods (order N^2) for systems with as few as one thousand charged particles (equivalent to 300 water molecules). Timings and accuracy estimates with system size N ($16 \leq N \leq 16000$) are given to illustrate the effectiveness and efficiency of the fmm.

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I. INTRODUCTION

Molecular dynamics and Monte Carlo simulations of electrolyte systems require the evaluation of the superimposed Coulomb fields of thousands particles (a mere 5 nm^3 of water contains approximately 4200 atoms). In this paper we describe the fmm of Greengard and Rokhlin [1-4] and its successful application to molecular dynamics simulations of aqueous systems including the calculation of electric polarization in model water systems. Specialization to interfacial problems of interest in electrochemistry is presented in outline only by way of a discussion of boundary conditions imposed by various interfaces.

A number of methods are in use to calculate long range Coulomb fields. Direct summation with a cut off after about 1.00 nm is common in many commercially available codes like Charmm [5] and Amber [6, 7]. Also available are empirical recipes like the Hingerty function [8] and other distance dependent dielectric 'constants' [6, 9]. A brief survey of empirical dielectric recipes in use in biological simulations has been given by Friedmann and Honig [10]. Widely used when rigor and accuracy and needed is the Ewald method [11-13]. Also there are a host of plane wise summation methods with origins in optics of crystals [14]. For homogeneous systems the reaction field method of Barker [15] is unrivaled for its simplicity and ease of use. Unfortunately this method is not easily applied to liquid-solid interfaces though attempts to extend it have been described [16, 17]. Ewald summation crudely applied is proportional to N^2 and at best $N^{3/2}$ where

N is the number of charges. The fast multipole method developed by Greengard and Rokhlin [1-4] is order N, and clearly the only viable method for large simulations. The fmm technique is also attractive for the ease of implementation of a variety of boundary conditions such as periodic, Dirichlet, Neumann and mixed boundaries. The method is a recursive algorithm based on multipole expansions for the evaluation of the Coulomb fields. The error in the algorithm is well controlled and can be made arbitrary small by increasing the number of terms retained in the multipole expansions. Additionally an adaptive version of the algorithm is available [3] in which regions of low or no charge density are not subdivided when the charge count falls below a specified integer. This results in considerable saving of computer time, and will make the code particularly useful in computations of aquated membranes and globular proteins.

The method has a number of advantages over direct and Ewald sum methods. As already mentioned it is an order N and hence faster for large number of particles (for a precision of 10^{-4} the cross over size varies from 30 to 1000 depending on boundary conditions). Also within the structure of the algorithm it is easy to impose a variety of boundary conditions. In contrast to Ewald methods no addition computational complexity is introduced by imposing boundary conditions. The method is also well suited to vector and parallel computation, allowing for the possibility of exploring very large systems.

II. DESCRIPTION OF THE FAST MULTIPOLE METHOD

In the calculations described later in this paper the three dimensional version of the fmm method is used to evaluate the electrostatic interaction, however for the purposes of describing the methods it suffices to consider the two dimensional version. The generalization to three dimensions is relatively straight forward.

Suppose simulation cell C contains N charged particles. The method divides C (which we will call a level 0 box) into four level 1 boxes. See Figure 1. These boxes are then subdivided into four more boxes creating an array of level 2 boxes. This process is repeated until some prescribed level L is reached. In Figure 1 displays L≈3. The finest level L is chosen to minimize computation and in doing so is proportional to log(N). The boxes formed by the division of a box are called children of the undivided 'parent' box. The far field due each to box at the finest level is calculated in terms of it's multipoles, up to order n. The precision of the method is set by the order n. Next the multipole moments of the parents are created from the children's moments by a linear transformation, starting at the finest level and working upward to level 0.

The strategy now will be to calculate a local expansion for each box that represents the far field potential. Beginning at level zero, the question is asked, which boxes are well separated from the main computational cell? The answer will depend on the boundary conditions. For a system with a 'free' boundary there are no well separated level 0 boxes because the there are no other level 0 boxes! For any periodic boundary condition it is the array of all images except adjacent images. The local expansion for the level zero box is found by transforming the multipole expansion of each of the well separated boxes. In the case of the free boundary this is trivial since there are no well separated boxes. However in the case of a periodic boundary condition there is an infinite number of image boxes. Fortunately in this case symmetry enables the local expansion to be calculated easily. The local expansion of a level 1 box can be considered to consist of two parts. One part representing particles included in the local expansion of the parent and another part for all particles in well separated boxes that are not present in the first part.
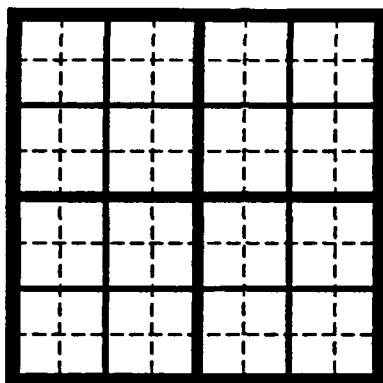
Figure 1. Schematic representation of the L = 3 subdivision of
the computational box C used in the fast multipole method.

The number of these well separated boxes is finite and bounded. The contribution to the local expansion by particles in the first part is simply found by transforming the origin of the parent's local expansion to the center of the box. The second part is calculated by transforming a finite number of multipole expansions. Once this procedure is applied to all level 1 boxes it is applied recursively to level 2 and so on. Finally a local expansion of all particles in well separated boxes is found for each box at the finest level. What remains to be done is to find the potential due to particles in adjacent boxes and this is calculated by doing a direct sum over particles in these boxes.

The Figure 2 schematically illustrates the two dimensional analogs of systems of interest in electrochemistry. Arrows show location of metal boundaries. In the first (a) the simulation cell is replicated throughout 2-space, to represent an infinite bulk fluid. In cases (b-d) it is replicated laterally in the x direction, however the y direction has to be handled differently in each case. In case b the system is a either an isolated ('free') film or one bounded by two low dielectric surfaces. In case c the film is bounded by two metals which require the inclusion of images boxes $\tilde{C}$ (generated from C by charge conjugation: $q \rightarrow -q$ and reflection in the xy plane: $z\text{-}z_0$ $\rightarrow z_0\text{-}z$). The bottom right case (d) represents an emersed electrolyte film of finite thickness on a metal electrode. In this case there is only one set of image boxes $\tilde{C}$

The implementation of these various boundary condition is straight forward in the fmm technique. For instance consider the periodic boundaries. In this case the cell C is replicated in space, as illustrated by Figure 2a. Since we know the multipole expansions for the cell C, we thereby know the expansions for each of the boxes in any image cell. To begin the calculation of the local expansion of cell C (i.e. the level 0 box) we need to sum over all transformations of the coefficients of well separated level 0 image boxes. To sum over all these transformations each time would be extremely costly in cpu time. However if we use the fact that the transformation operator is a linear operator and the coefficients of each cell are identical then we need only sum over all the coefficients to find a new operator that then can be applied to the multipole coefficients of cell C (at level 0) in order to find the local expansion coefficients of cell C. The beauty of this approach is that this operator is independent of the particle positions and therefore only needs to be calculated once in a lifetime.
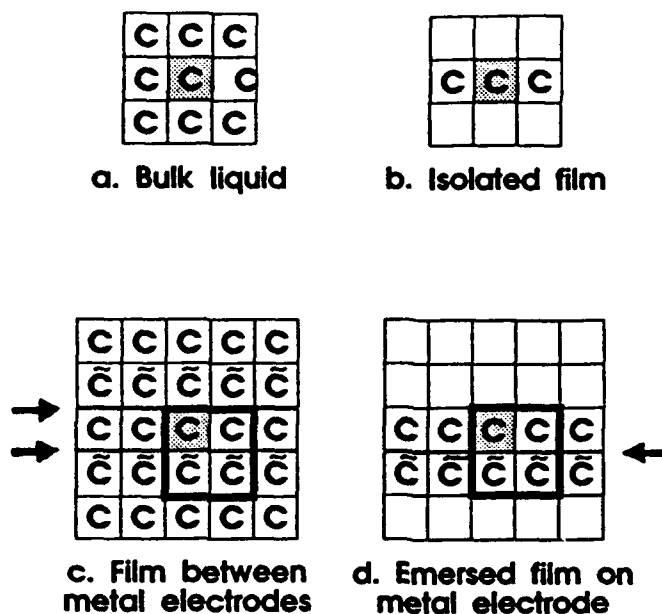
Figure 2. Two dimensional analogs of boundary conditions frequently met in molecular dynamics simulations of electrochemical systems. Arrows show location of metal boundaries.

In the case of an isolated film as illustrated in Figure 2b, the same approach as describe above will work. The only difference is that the sum over transformation operators is restricted to a single row. So the summed operator will be different from above but still only needs to be calculated once in a lifetime. The introduction of metal boundaries introduces images that are related to the root cell by charge conjugation and inversion operations. For example consider Figure 2c, where a periodic film is constrained between two metal plates. The images cells now consists of alternating rows of C and $\tilde{C}$ cells. By considering the heavily outline box as the primitive cell in the system, the system is mapped back to a fully periodic system. One may be tempted to use the summed operator that was calculated for the case 2a, however one needs to be concerned with the conditional convergence of the operator sums. In case 2a the appropriate order is to sum over spherical shells, since one may argue that the physical system is rotationally invariant even though the replicated lattice of cells is cubic (in 3-space) or square (in 2-space). However in case 2c the isotopic symmetry has been broken by the metal plates and the sums must be performed in slab fashion. The case illustrated by Figure 2d can be mapped to case 2b.

III. VALIDATION

In this section the fmm method will be compared with other methods for evaluating electrostatic interactions. The comparisons are made among eleven systems spanning three orders of magnitude in size N and with three different boundary conditions:

1) free boundaries
2) periodic in x,y,z
3) periodic in x and y and free the z direction.

For these comparisons as well as the rest of the paper, this implementation of fmm method retained the set of spherical harmonics (Y_{nm} | $0 \le n \le 7$) in all expansions. This typically results in a relative accuracy of the order of 10^{-4} The number of levels was chosen to minimize the computation time and is dependent on the number of particles. To a good approximation this minimum is found at $L = \log_8(N/64)$.

For free boundaries the fmm is compared with direct summation methods. For the purpose of this comparison it is assumed that the direct method is exact (actually only accurate to 10^{-15}). For the fully periodic system the comparison is made with the standard three dimensional Ewald method. In the two dimensional periodic system the two dimensional slab Ewald method of Rhee et al [18] is used for comparison. In the periodic systems (two and three dimensional) the accuracy of the Ewald method is controlled by the number of terms in the real and reciprocal space sums. Using a simple estimate of the error the cutoff radius in real and reciprocal space was chosen to achieve an accuracy of approximately 10^{-4}. To test the accuracy of both the fmm and Ewald methods a high accuracy Ewald method was used. All the algorithms were coded in double precision and run on an IBM RS6000 model 540 workstation.

To compare the methods an N particle test system was generated by choosing from a uniform random distribution on the interval ($-\frac{1}{2},\frac{1}{2}$) the charge and x,y,z coordinates of each of the particles. The systems are made neutral by adding a constant correction to each charge. In Table 1 the cpu time t, absolute relative error in the energy e_E, and rms deviation of the force e_F are listed for the various methods. The cpu time t is in seconds and e_F is defined as,

$$e_F = \sqrt{\sum_i (f_i^{method} - f_i^{exact})^2 \Big/ \sum_i (f_i^{exact})^2} \qquad (1)$$

The far right hand column of table 1 list the number of levels L used in the fmm calculation. At the end of the table is a summary of a fit of the execution time to the form $t = AN^\beta$. The coefficient β for the fmm method is close to one, as predicted, for all the boundary conditions. In fact the deviation from one can be traced to surface to volume effects. From the fitting parameters a critical size N_c at which the fast fmm method becomes most efficient is estimated and it too is listed at the end of table 1. The estimate of $N_c = 17$ for the two dimensional slab boundary conditions is lower than the actual cross over value of 30, but the discrepancy can be traced to surface to volume effects as well. As expected for large systems the fmm is much more efficient than direct or Ewald methods. In particular for systems with finite geometry in one or more dimensions, as in the two dimensional slab case the fmm is clearly superior to Ewald methods.

| N | | | free | | periodic 3d | | periodic 2d | | L |
			Direct	fmm	Ewald	fmm	Ewald	fmm	
16	t		0.0	0.11	0.0	0.102	0.02	0.09	0
	e_E		0.0	0.0	1×10^{-4}	3×10^{-5}	2×10^{-5}	7×10^{-5}	
	e_F		0.0	0.0	3×10^{-4}	6×10^{-5}	1×10^{-4}	1×10^{-4}	

N		free		periodic 3d		periodic 2d		L
		Direct	fmm	Ewald	fmm	Ewald	fmm	
32	t	0.0	0.10	0.010	0.153	0.12	0.10	0
	e_E	0.0	0.0	2×10^{-4}	4×10^{-5}	4×10^{-5}	6×10^{-6}	
	e_F	0.0	0.0	8×10^{-4}	2×10^{-4}	3×10^{-4}	2×10^{-4}	
63	t	0.0	0.11	0.034	0.22	0.41	0.14	0
	e_E	0.0	0.0	6×10^{-4}	1×10^{-5}	5×10^{-5}	1×10^{-5}	
	e_F	0.0	0.0	6×10^{-4}	1×10^{-4}	2×10^{-4}	2×10^{-4}	
125	t	0.02	0.17	0.14	0.36	1.7	0.24	1
	e_E	0.0	0.0	4×10^{-3}	2×10^{-4}	4×10^{-4}	3×10^{-4}	
	e_F	0.0	0.0	3×10^{-4}	6×10^{-5}	2×10^{-4}	2×10^{-4}	
250	t	0.07	0.26	0.48	0.57	6.4	0.37	1
	e_E	0.0	0.0	2×10^{-5}	4×10^{-5}	9×10^{-4}	2×10^{-4}	
	e_F	0.0	0.0	6×10^{-4}	9×10^{-5}	2×10^{-4}	2×10^{-4}	
500	t	0.29	0.53	1.58	1.34	25.8	0.95	1
	e_E	0.0	0.0	7×10^{-5}	3×10^{-5}	1×10^{-5}	1×10^{-5}	
	e_F	0.0	0.0	5×10^{-4}	7×10^{-5}	5×10^{-5}	6×10^{-5}	
1000	t	1.12	1.28	5.9	2.6	105	1.88	2
	e_E	0.0	1×10^{-5}	1×10^{-5}	7×10^{-5}	1×10^{-4}	1×10^{-5}	
	e_F	0.0	3×10^{-5}	2×10^{-4}	5×10^{-5}	1×10^{-4}	1×10^{-4}	
2000	t	4.6	2.3	21.5	4.2	410	3.4	2
	e_E	0.0	1×10^{-5}	2×10^{-4}	4×10^{-5}	2×10^{-5}	3×10^{-5}	
	e_F	0.0	3×10^{-5}	3×10^{-4}	7×10^{-5}	1×10^{-4}	1×10^{-4}	
4000	t	18.3	6.2	78	10.4			2
	e_E	0.0	1×10^{-6}	7×10^{-6}	2×10^{-5}			
	e_F	0.0	3×10^{-6}	8×10^{-5}	6×10^{-6}			
8000	t	73	14	255	21.5			3
	e_E	0.0	3×10^{-5}	1×10^{-4}	4×10^{-5}			
	e_F	0.0	1×10^{-4}	5×10^{-5}	2×10^{-6}			

Table 1. The cpu time t in seconds for an IBM workstation RS6000/540, relative error e_E in energy and the RMS value of the relative error e_F in the force.

N			free		periodic 3d		periodic 2d		L
			Direct	fmm	Ewald	fmm	Ewald	fmm	
16000		t	310	26	950	35			3
		e_E	0.0	3×10^{-5}	2×10^{-4}	2×10^{-4}			
		e_F	0.0	1×10^{-4}	2×10^{-4}	6×10^{-6}			
Fit		A	1.636×10^{-6}	7.234×10^{-4}	1.839×10^{-5}	2.905×10^{-3}	1.077×10^{-4}	1.774×10^{-3}	
		β	1.960	1.084	1.835	0.976	1.994	0.995	
		N_c	1069		393		19		

IV. APPLICATION TO ELECTROCHEMICAL SYSTEMS

Electrochemical systems prevade nature. At the simplest level they can be visualized as a collection of polar entities held together by electrostatic interactions and held apart by the Pauli repulsion interaction of their constituent electrons. Coulomb interactions being essentially long range in nature, control the fluctuations in electric polarization that manifest as the dielectric constant. Since a major component of the total interaction energy is electrostatic it is essential to compute this part accurately if polarization effects are important. In the light of these introductory comments it is appropriate that we demonstrate the power of the fmm code as implemented by us, in a calculation of the dielectric constant. First however it is necessary describe briefly the models and interaction potentials used in these studies.

The spce water model [19]. In this model water is represented as a lennard-jones atom centered or the oxygen atom O with $\sigma = 0.3160$ nm, $\varepsilon = 0.6502$ kJ/mol. Embedded in the sphere are two point masses H carrying charge q=0.4238|e| in electron units. The HOH bond angle is 109.5° and the OH bond length is 0.1 nm.

The total interaction energy. The Coulomb interaction between molecules was represented as sum of $1/r$ interactions between all point charges. The short range part of the intermolecular interaction was modeled by a lennard-jones potential between the O atoms of each water, and smoothly truncated to zero at $R = 0.72$ nm by the function T defined below. The electrostatic coupling constant K had the value 138.936 KJ·nm/(mole· e^2) in the units used in this calculation. The complete interaction energy U is,

$$U = \sum_{\substack{\alpha \in A_i \\ \beta \in A_j \\ i < j}} \left(\frac{Kq_\alpha q_\beta}{r_{\alpha\beta}} + 4\varepsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}} \right)^6 \right] T(R_{ij}) \right) \qquad (2)$$

where i and j are molecular indices, and, α and β are atomic indices. The symbol A_i represents the set of all atoms of molecule i. The symbol R_{ij} is the distance between the center of mass of molecules i and j. The symbol $r_{\alpha\beta}$ is the distance between atoms α and β.

The form of the truncation function T is given by,

$$
T(R) = \left[\begin{array}{ll} 1 & R < R_L^T \\ \left(1 - \left(\dfrac{R - R_L^T}{R_U^T - R_L^T} \right)^m \right)^n & R_L^T < R < R_U^T \\ 0 & R_U^T < R \end{array} \right. \tag{3}
$$

where $R_L^T=0.68$ nm and $R_U^T=0.72$ nm. The intege $\cdot$ m and n control the smoothness of the truncation function at R_L^T and R_U^T respectively. In this calculation $n = m = 2$ which insured that energy was smooth up to and including first spatial derivatives.

Bond lengths and angles were explicitly cr istrained by a quaternion formulation of the rigid body equations of motion [20-22]. The equations of motion were expressed as a set of first order differential equations and a fourth order multi-step numerical scheme was used to integrate them in time steps of 2 fs. At each time step a small scaling correction was made to the quaternions and velocities to correct global drift. Additionaly the global center of mass velocities in the x, y and z directions were set to zero at each time step by shifting the molecular translational velocities.

V. DIELECTRIC CONSTANT OF WATER

As a test of the fast multipole method in an actual molecular dynamics simulation we used it to evaluate the dielectric constant of water in bulk. There h.. ve been numerous simulations of water dielectric constants. Unfortunately many omit important details that make it impossible to repeat the calculation. There are however a few that have provided these details and we have selected one clear enough to make comparisons. Previously Reddy and Berkowitz [23] used the reaction field method to estimate dielectric constant of spce water. In this study we have used both fmm and Ewald techniques to estimate dielectric constant of spce water. As necessary with all simulations of Coulomb fields the boundary conditions at infinity need to be clearly specified. We have assumed that the primitive cell has been periodically replicated to fill a sphere with very large radius. Outside of the sphere space is assumed to be filled with a perfect conductor. The appropriate fluctuation expression for the dielectric constant of the system with this boundary conditions is:

$$
\epsilon = \frac{<M^2>}{3VkT} + \epsilon_0 \tag{4}
$$

where M is the total polarization of the sample and ϵ_0 is the dielectric constant of a vacuum. The simulations where done for systems containing 27, 64, 125 and 216 spce water molecules at temperature of 298K and 361K. All the simulations ran for at least 1 ns except for the 27 and 64 molecule systems at 361K which were integrated 0.5 ns. In the simulations at the higher temperature 361K we evaluated coulomb fields by fmm and Ewald techniques in order to directly compare the two methods. In estimating the errors in the dielectric constant the temporal correlation between the polarization of different samples is important. In this study configura-

tions were stored every 0.1 ps and then binned. For large bin sizes the samples should be statically independent. This was tested by examining the variance of the average polarziation as a function of bin size. If this appeared to be approaching an asymptotic value then the bin size was deemed to be large enough and the asymptotic value of the variance was used to estimate the error in ε. Using this method we found agreement between the fmm and Ewald methods for the size of the error. However our error estimate was much larger that the error estimates given by Reddy and Berkowitz [23] for runs of similar length in their reaction field study. However the method they used to determine the error is not clear from reading their paper.
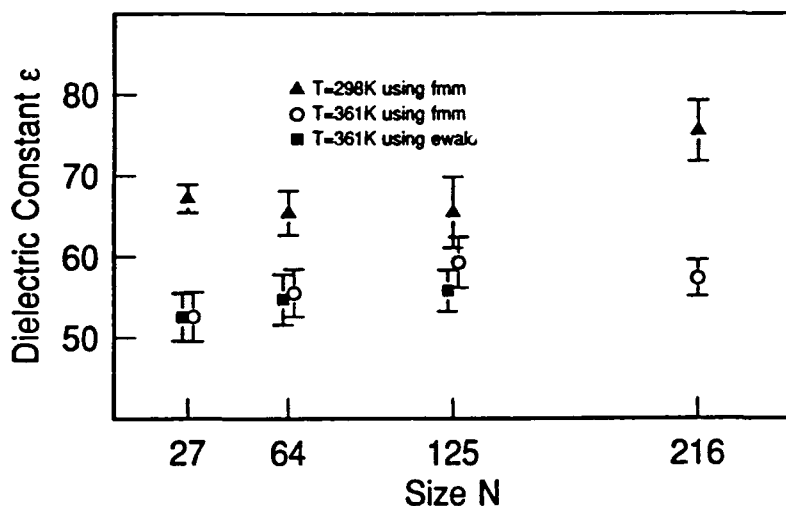

Figure 3. The dependence of the relative dielectric constant $\varepsilon/\varepsilon_0$ of spce water on the number N of molecules in the primative simulation cell.

Figure 3 shows a plot of dielectric constant versus size N the number of spce water molecules in the basic simulation cell for two temperatures. The different data symbols refer to the results from using fmm and Ewald methods to evaluate the electric forces acting on the charges. Otherwise the two codes were identical. The first thing to note is that the fmm and Ewald techniques agree within statistical error. The 216 molecule simulation with fmm can be compared to Reddy and Berkowitz [23] reaction field simulation. Using fmm the value $\varepsilon=75.5\pm5\%$ at T=298K and $\varepsilon=57.3 \pm 4\%$ at T=361K is found for the dielectric constant of the spce water model. In the reaction field study $\varepsilon(T=298K)=70.7\pm1\%$ and $\varepsilon(T=373K)=51 \pm .7\%$. Using a linear interpolation this would correspond to of $\varepsilon=54.1$ at 361K. At the higher temperature T=361K there appears to be only weak size dependence, whereas at T=298K the size dependence is clearly apparant especially in the range from 125 to 216 molecules. The calculated values agree well with experimental values [24].

VII. CONCLUSIONS AND OUTLOOK

This paper described the first electrochemical application of the fast multipole method in a molecular dynamics calculation of the dielectric constant. The fast multipole method provides a fast and accurate technique for the evaluation of electrostatic interactions and clearly is the prefered method in systems with large numbers of charged particles. In a system of 216 spce water molecules, which has 648 charges, the fmm took 62% of the time of an Ewald method of the same accuracy. For 512 spce waters fmm takes only 30% of the time for Ewald. The method is well suited to handle a variety of boundary conditions. Given that this method is available in adaptive and parallelizable versions it is a very powerful tool for use in classical simulations of systems with aqueous phases. Important future applicatons will not be confined just to electrolytes in the bulk or at planar surfaces. It is quite obvious that the method can be used in simulations where water surrounds or is confined by irregular boundaries as are frequently encountered in biological systems.

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